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| (54) Title: ELECTRODIALYSIS APPARATUS (57) Abstract An electrodialysis apparatus for purifying water is described. The apparatus has an anode chamber and cathode chamber, and is characterised in that each of said anode and cathode chambers contains a porous bed of ion exchange material. There are preferred flow directions through each chamber. The electrodialysis apparatus of the present invention does not require the addition of acid or alkali to the electrode chambers and relies on water splitting at the electrodes for the generation of hydronium and hydroxide ions for replenishing the ion exchange resins within the electrode compartments and for assisting in driving out the ionic impurities from the desalting stream flow paths into the concentrating stream. Two or more electrodialysis apparatus could be combined to form a polyelectrodialysis apparatus. | | |

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Electrodialysis Apparatus

The present invention relates to an electrodialysis apparatus for purifying water and also embraces a method of electrodialysis.

As will be well known to those skilled in the art, electrodialysis comprises passing a desalting stream of water to be purified between an anode and a cathode. Perm-selective membranes are positioned between the desalting stream and the electrodes, such that cations migrating towards the cathode pass through a cation selective membrane, whilst anions migrating towards the anode pass through an anion perm-selective membrane. As electrodialysis proceeds, the water to be purified is progressively depleted of ions. In some instances, an ion exchange resin bed is placed in the desalting stream, and this has the advantage of maintaining the electrical conductivity of the water to be purified as deionisation proceeds. Electrodialysis in which an ion exchange resin bed is used in the water to be purified is known as electrodeionisation.

US-A-3645884 (Gilliland) discloses a five compartment electrodeionisation cell comprising outer anode and cathode compartments and a central concentrating compartment. A desalting compartment is positioned between each electrode compartment and the central concentrating compartment. The desalting compartment nearest the anode is separated from the anode chamber and from the central concentrating compartment by two, respective cation selective membranes. Similarly, the desalting compartment nearest the cathode is separated from the cathode chamber and from the concentrating compartment by two, respective anion selective membranes.

In operation, water to be purified is passed through the two desalting compartments in succession, and a voltage is applied across the anode and cathode, such that cations are caused to migrate from the water to be purified in the desalting compartment nearest the anode into the central concentrating compartment, and anions are caused to migrate from the water to be purified in the desalting compartment nearest the cathode into the concentrating compartment. Each of the desalting compartments comprises a porous bed of ion exchange material.

According to US-A-3645884, the anode compartment is filled with a weakly acidic solution, whilst the

1 cathode department is filled with a weakly alkaline solution. Thus, in operation, hydronium ions from
2 the anode compartment are caused or allowed to pass into the adjacent desalting compartment to assist
3 in driving out the cation impurities in the water to be purified. Analogously, hydroxide ions in the
4 cathode compartment are caused or allowed in use to pass into the juxtaposed desalting compartment
5 to assist in driving out the anion impurities from the desalting stream into the central concentrating
6 chamber.

7
8 US-A-3645884 discloses that when a 0.085N sodium chloride solution is deionised for a period of two
9 hours by impressing a current of 12 amperes at 10 to 20 volts across the ion exchange beds, a final
10 product having a sodium chloride concentration of 0.0085N is achieved, indicating a 90% removal of
11 ions from the water to be purified. The final product water has a conductivity of 1025 $\mu\text{S}/\text{cm}$ at 25°C.

12

13 It is an object of the present invention to provide an improved electrodialysis apparatus.

14

15 In particular, it is an object of the present invention to provide an electrodialysis apparatus which is
16 capable of producing highly-purified water, that is water having a conductivity of less than 0.20 $\mu\text{S}/\text{cm}$,
17 i.e. a resistivity of at least 5M Ω -cm and, under suitable operating and feed conditions, of at least
18 15M Ω -cm i.e. a conductivity of less than 0.067 $\mu\text{S}/\text{cm}$ at 25°C.

19

20 According to one aspect of the present invention therefore there is provided an electrodialysis
21 apparatus for purifying water, which apparatus comprises means defining an anode chamber, means
22 defining a cathode chamber, an anode means disposed within the anode chamber, a cathode means
23 disposed within said cathode chamber, means defining a desalting stream flow path between said anode
24 and said cathode means, means defining a concentrating stream flow path adjacent said desalting
25 stream flow path, means for causing or allowing water to be purified to flow within the desalting
26 stream flow path and means for causing or allowing a fluid adapted to receive ionic impurities from the
27 water to be purified to flow within the concentrating stream flow path; wherein said desalting stream
28 flow path comprises a first portion juxtaposed the anode means and a second portion juxtaposed said
29 cathode means, and said means defining the desalting stream flow path comprises two first partition
30 means that separate the first portion of the desalting stream flow path from the anode chamber and the
31 concentrating stream flow path respectively, which first partition means are selectively permeable to
32 cations and are spaced apart on an axis between said anode means and cathode means, and two second

1 partition means that separate the second portion of the desalting stream flow path from the cathode
2 chamber and the concentrating stream flow path respectively, which second partition means are
3 selectively permeable to anions and are spaced apart on said axis; characterised in that each of said
4 anode and cathode chambers contains a porous bed of ion exchange material.

5
6 In some embodiments, the cathode chamber may contain anion exchange resin. Said anode chamber
7 may contain cation exchange resin.

8
9 In another aspect of the present invention there is provided a method of electrodialysis comprising
10 causing or allowing water to be purified to flow in the desalting stream flow path of an electrodialysis
11 apparatus in accordance with the present invention, causing or allowing a fluid adapted to receive ionic
12 impurities from said water to be purified to flow within the concentrating stream path and applying a
13 voltage across the anode means and cathode means.

14
15 In some embodiments, substantially pure water may be caused or allowed to flow in the anode and/or
16 cathode chamber, and preferably substantially pure water is used in both the anode chamber and the
17 cathode chamber. By "substantially pure water" is meant water having a resistivity of at least $1\text{M}\Omega\text{-cm}$
18 cm, preferably at least $15\text{M}\Omega\text{-cm}$.

19
20 It has been found that the electrodialysis apparatus of the present invention can be used to produce
21 high purity water, that is water having a resistivity of at least $15\text{M}\Omega\text{-cm}$.

22
23 Conveniently, the substantially pure water used within the anode and/or cathode chamber may be
24 water that has been purified using the apparatus of the invention. Typically, means may be provided
25 for supplying water that has been purified in the desalting stream flow path to the anode and/or
26 cathode chamber. It is also envisaged that in some cases, the water used in one or both of the
27 electrode chamber may be recycled through a secondary purifier, e.g. a second electrodialysis or
28 electrodeionisation device.

29
30 Preferably the fluid supplied to the concentrating stream flow path is also substantially pure water, and
31 in some embodiments means may be provided for supplying substantially pure water that has been
32 purified within the desalting stream flow path to the concentrating stream flow path. However, the

1 invention also embraces the use of water of lower quality in the concentrating stream flow path.

2

3 The electrodialysis apparatus of the present invention does not require the addition of acid or alkali to
4 the electrode chambers and relies on water splitting at the electrodes for the generation of hydronium
5 and hydroxide ions for replenishing the ion change resins within the electrode compartments and for
6 assisting in driving out the ionic impurities from the desalting stream flow paths into the concentrating
7 stream.

8

9 In some embodiments, water that has been purified within the desalting stream may be caused or
10 allowed to flow in parallel through the concentrating stream and at least one of the anode and cathode
11 chambers. Alternatively, the substantially pure water may be caused or allowed to flow successively
12 through at least one of the anode and cathode chambers and then through the concentrating stream
13 flow path. Preferably, the fluid within the concentrating stream is caused or allowed to flow counter-
14 current to the flow of water to be purified in at least one of the first and second portions of the
15 desalting streams flow paths. Preferably the water within at least one of the anode and cathode
16 chambers is caused or allowed to flow counter-current to the flow of water to be purified in at least
17 one of said first and second portions.

18

19 Said concentrating stream flow path may contain a porous bed of ion exchange material.

20

21 Usually the desalting stream flow path will contain a porous bed of ion exchange material. Said first
22 portion may contain cation exchange resin, and said second portion may contain anion exchange resin.

23

24 The water to be purified may be passed through the first and second portions of the desalting stream
25 flow path in any order, although preferably the water to be purified is passed through the first portion
26 first, followed by the second portion. In this way, the water to be purified is acidified in the first
27 portion by the presence of hydronium ions generated by water splitting at the anode. The water to be
28 purified is thus slightly acidic when it enters the second portion which contains hydroxide ions
29 produced at the cathode. This arrangement, as will be appreciated by those skilled in the art, will assist
30 in reducing the build-up of scale in the apparatus.

31

32 It is envisaged that in some embodiments the water to be purified may be passed in succession through

1 two or more electrodeionisation apparatus according to the present invention.

2

3 In another aspect of the present invention therefore there is provided polyelectrodialysis apparatus
4 comprising two electrodialysis apparatus in accordance with the present invention. In some
5 embodiments, one of the electrodes of the polyelectrodialysis apparatus in accordance with the
6 invention may be shared by both electrodialysis apparatus. The polyelectrodialysis apparatus may
7 comprise a single anode or cathode that is common to both electrodialysis apparatus.

8

9 Where the water to be purified passes through two electrodialysis apparatus in accordance with the
10 present invention, it is preferred that the water to be purified passes successively through the first and
11 second portions of the first electrodialysis apparatus, and then through the second and first portions in
12 succession of the second electrodialysis apparatus, so that the water to be purified is given a final
13 polish by passage through a cation exchange resin bed.

14

15 Following is a description by way of example only with reference to the accompanying drawings of
16 embodiments of the present invention.

17

18 In the drawings:

19

20 Figure 1 is a flow diagram of a first electrodialysis apparatus in accordance with the present
21 invention;

22 Figure 2 is a flow diagram of a second electrodialysis apparatus in accordance with the present
23 invention;

24 Figure 3 is another flow diagram of a third electrodialysis apparatus in accordance with the
25 present invention;

26 Figure 4 is a flow diagram of a first polyelectrodialysis apparatus in accordance with the
27 present invention; and

28 Figure 5 is a flow diagram of a second polyelectrodialysis apparatus in accordance with the
29 present invention.

30

31 With reference to Figure 1, a first electrodialysis apparatus 10 in accordance with the present invention
32 comprises an anode 14 and a cathode 16 that is spaced from the anode. Said anode, which may be a

1 platinum coated anode, is accommodated within an anode compartment 24 and said cathode 16 is
2 accommodated within a cathode compartment 26. Intermediate said anode and cathode compartments
3 24, 26 the apparatus 10 comprises three further compartments, namely a first desalting compartment
4 36 adjacent the anode compartment 24, a second desalting compartment 46 adjacent the cathode
5 compartment 26 and a concentrating compartment 28 interposed between said first and second
6 desalting compartments 36, 46.

7
8 Said anode compartment 24 is partitioned from the first desalting compartment 36 by a first cation
9 perm-selective membrane 32 and said first desalting compartment 36 is partitioned from the
10 concentrating compartment 28 by a second cation perm-selective membrane 34. Similarly said
11 cathode compartment 26 is partitioned from the second desalting compartment 46 by a first anion
12 perm-selective membrane 42, and said second desalting compartment 46 is partitioned from the
13 concentrating compartment 28 by a second anion perm-selective membrane 44.

14
15 The construction of electrodialysis apparatus of this kind will be generally well known to those skilled
16 in the art and has been described inter alia in numerous prior patent specifications (see, e.g. GB-A-
17 769307, EP-A-0078842, EP-A-0170895). It is envisaged that said apparatus will conveniently
18 comprise a stack of juxtaposed compartment-forming elements of predetermined thickness with said
19 ion selective membranes 32, 34, 42, 44 interposing between neighbouring elements. Said electrodes
20 14, 16 will be formed as thin plates or screens and each will be interposed between an electrode
21 compartment-forming element and an adjacent end plate.

22
23 Each compartment-forming element may be manufactured from a thermoplastic material and will be
24 formed with a large, central opening that extends through the element and forms a compartment, with
25 the body of the element defining the outer perimeter of the compartment. The elements may further be
26 drilled or moulded with one or more through-bores around the central opening. In the assembled
27 stack these bores will align with corresponding bores in the juxtaposed elements to form ports for
28 conveying fluids between compartments interiorly of the stack. The ends of each compartment will be
29 closed in the assembled stack by the neighbouring membranes. An end plate will be provided at each
30 end of the stack, and the assembly will be held together by such means as a plurality of bolts that
31 extend between the end plates, through aligning apertures formed in all of the elements. Compressible,
32 fluid-tight seals will typically be interposed between each element/plate and the neighbouring

1 membranes, which seals will be compressed by drawing the end plates together tightly by means of the
2 bolts. As this kind of construction will be generally familiar to those skilled in the art, no further
3 description of it is given herein.

4

5 In the electrodialysis apparatus of the present invention the thickness of each of the desalting
6 compartments 36, 46 in the electrode-electrode direction may be in the range 5 to 40mm, and the
7 thickness of the electrode and concentrating compartments 24, 26, 28 may be in the region of 2 to
8 30mm.

9

10 The anode compartment 24 of the apparatus of Figure 1 contains a porous bed of cation exchange
11 resin 25, and the cathode compartment 26 contains a porous bed of anion exchange resin 27. As
12 cation exchange resin may be used any suitable resin known to those skilled in the art such as, for
13 example, that which is commercially available from Dow Liquid Separations under the trade mark
14 DOWEX MARATHON C. Said anion exchange resin may similarly be any suitable resin known to
15 those skilled in the art such, for example, a DOWEX MARATHON A.

16

17 Said first desalting compartment 36 also contains a porous bed of cation exchange resin 37 and said
18 second desalting compartment 46 contains a porous bed of anion exchange resin 47. Said
19 concentrating compartment 28 also contains a porous bed of ion exchange resin 29 which may be
20 cation exchange resin, anion exchange resin or a mixture of both of these.

21

22 Each of the compartments 24, 26, 28, 36, 46 is provided with an inlet and an outlet. In use the inlet to
23 the first desalting compartment 36 is connected to a supply 50 of water to be purified.

24

25 Internal porting (not shown) may be included to connect the outlet of the first desalting chamber 36 to
26 the inlet of the second desalting chamber 46, and the inlets/outlets of the desalting chambers 36, 46
27 may be arranged such that the water to be purified flows in the same direction through both desalting
28 chambers as shown in Figure 1.

29

30 Substantially pure water, that is water having a purity of at least $1\text{M}\Omega\text{-cm}$ is supplied to each of the
31 electrode chambers 24, 26 and may also be supplied to the concentrating chamber 28 to provide
32 respectively electrode chamber streams 52, 54 and a concentrating, flushing stream 56.

1

2 In use, an operating voltage of 2 to 100V is applied across the anode 14 and cathode 16 sufficient to
3 obtain water splitting at the electrodes. Cations in the water to be purified are taken up on the cation
4 exchange resin 37 in the first desalting chamber 36, being replaced in solution by hydronium ions.
5 Hydronium ions generated at the anode 14 pass via the first cation exchange membrane 32 into the
6 cation resin bed under the influence of the applied electrical potential. As they pass through the cation
7 resin bed, the hydronium ions regenerate the cation exchange resin by being exchanged for cations
8 from the water to be purified 50. The hydronium ions and the impurity cations pass via the second
9 cation exchange membrane 34 into the concentrating chamber 28 from which they cannot proceed
10 further towards the cathode 16 owing to the presence of the second anion selective membrane 44.
11 The cations are thus eluted from the concentrating chamber 28 by the action of the high purity
12 "flushing" stream 56 flowing through the concentrating chamber 28.

13

14 In a similar manner, anions in the water to be purified are carried to the concentrating chamber 28
15 under the influence of the cathode-generated hydroxide ions and the electrical potential, via the anion
16 exchange resin 47 in the second desalting chamber 46 and the second anion selective membrane 44.
17 The impurity anions are also eluted by the flushing stream 56 within the concentrating chamber 28.
18 The product water 60 is delivered from the outlet of the second desalting chamber 46.

19

20 Figure 2 shows a second electrodialysis apparatus in accordance with the invention which is suitable
21 for use on a small scale. Many of the components of the apparatus of Figure 2 are common to the
22 apparatus of Figure 1 and, for these, the identical reference numerals as used in Figure 1 are used. It
23 will be seen that the electrodialysis apparatus of Figure 2 differs from that shown in Figure 1 in that the
24 first desalting chamber 36 is divided by means of internal partitions 52 into two sub-chambers 36a,
25 36b.

26

27 The water to be purified 50 is supplied in succession to one of the sub-chambers 36a of the first
28 desalting compartment 36, then to the second desalting compartment 46 and finally to the second sub-
29 chamber 36b of the first desalting compartment 36. The water to be purified 50 is thus passed in
30 succession through a cation exchange resin bed, an anion exchange resin bed and finally a cation
31 exchange resin bed which gives the water to be purified a final, polishing treatment. As is also
32 apparent from Figure 2, a portion of the product water 60 is supplied in parallel to the electrode

1 chambers 24, 26 and to the concentrating chamber 28. Although not shown in Figure 2, internal
2 porting is conveniently provided in the stack to make the necessary connections between the various
3 chambers. Each of the desalting compartments 36a, 36b, 46 of the electro dialysis apparatus of Figure
4 2 has a thickness of 8mm in the electrode-electrode direction. The widths of the electrode
5 compartments 24, 26 and the concentrating compartment 28 are each about 5mm.

6
7 Those skilled in the art will appreciate that the highest purity water of the flushing stream is thus
8 allowed to flow through the anode chamber 24 and concentrating chamber 28 juxtaposed the flow
9 through the second sub-chamber 36b of the first desalting compartment 36, so that the highest purity
10 water is flowing juxtaposed the water to be purified 50 just before it exits the apparatus as product 60.

11
12 It has been found that when the electro dialysis apparatus of Figure 2 is used to treat recirculating water
13 from a tank having an initial conductivity of 15 to 20 μ S-cm, a final purity of 17M Ω -cm can be
14 achieved.

15
16 A third electro dialysis apparatus in accordance with the present invention is illustrated in Figure 3. The
17 construction of the third electro dialysis apparatus is similar to that of the second electro dialysis
18 apparatus illustrated in Figure 2, and accordingly the same reference numerals will be used for like
19 parts as before. The difference between the second and third electro dialysis apparatus resides in the
20 flow path of the electrode and concentration streams through the apparatus.

21
22 In the third electro dialysis apparatus illustrated in Figure 3, a portion of the product stream 60 is
23 returned through the apparatus and is directed to flow through the anode chamber 24, the cathode
24 chamber 26 and the concentrating chamber 28 in succession. It will be seen from Figure 3 that the
25 streams through the electrode chambers 24, 26 are directed to flow in the same direction as one
26 another, with the stream through the concentrating chamber 28 flowing in the opposite direction.

27
28 Figure 4 shows a first polyelectro dialysis apparatus 100 in accordance with the present invention. This
29 apparatus comprises two electro dialysis apparatus 10, 10' of the kind described above with reference
30 to Figure 1. The components of each electro dialysis apparatus 10, 10' of the polyelectro dialysis
31 apparatus of Figure 4 that are the same as or similar to the components of the electro dialysis apparatus
32 of Figure 1 are indicated by the same reference numerals as used in Figure 1, with the prime being used

1 to indicate components of the second electro dialysis apparatus 10'.

2

3 As can be seen from Figure 4, the water to be purified 50 is supplied firstly to the first desalting
4 chamber 36 of the first electro dialysis apparatus 10 and then, through internal porting (not shown), to
5 the second desalting chamber 46 of the first electro dialysis apparatus 10. The outlet 50' of the second
6 desalting chamber 46 of the first electro dialysis apparatus 10 is connected to the second desalting
7 chamber 46' of the second electro dialysis apparatus 10', and internal porting (not shown) within the
8 second electro dialysis apparatus 10' is provided to supply the feed from the second desalting chamber
9 46' to the first desalting chamber 36'. The water to be purified 50 is thus passed successively through a
10 cation exchange resin bed 36, a first anion exchange resin bed 46, a second anion exchange resin bed
11 46' and finally a second cation exchange resin bed 36' for polishing. The product water 60 is delivered
12 from the outlet of the first desalting chamber 36' of the second electro dialysis apparatus 10'.

13

14 Conversely, the electrode streams 52, 54, 52', 54' and the concentrating streams 56, 56' are supplied
15 firstly to the second electro dialysis apparatus 10' and subsequently to the first apparatus 10. This
16 assists in reducing the back diffusion of impurity ions from the electrode/concentrating streams into
17 the desalting stream.

18

19 As can be seen from Figure 4, the electrode streams 52, 54 exiting the first electro dialysis apparatus 10
20 are combined to provide an input stream 71 to a secondary purifier 70. Said secondary purifier 70 may
21 be any suitable water purifier known to those skilled in the art, although a further electro dialysis
22 apparatus or polyelectro dialysis apparatus in accordance with the present invention is preferred. Said
23 secondary purifier 70 has an output stream 72 which is used to feed the electrode streams 52', 54' of
24 the second electro dialysis apparatus 10'.

25

26 In the apparatus shown in Figure 4, each of the desalting chambers 36, 46, 36', 46' has a thickness in
27 the electrode-electrode direction of about 15mm, and each of the electrode and concentrating
28 chambers 24, 26, 28, 24', 26', 28' has a thickness of about 15mm.

29

30 It has been found that when operating the polyelectro dialysis apparatus as illustrated in Figure 4 for
31 over 2000 hours at a flow rate of 1.0 l/min of water of 12 to 15 $\mu\text{S}/\text{cm}$, water having a resistivity of
32 16.9 to 17.2 $\text{M}\Omega\text{-cm}$ at 25°C is produced.

1
2 A second polyelectrodialysis apparatus is illustrated in Figure 5. This second apparatus comprises two
3 juxtaposed electrodialysis apparatus of the kind hereinbefore described with reference to Figure 1. The
4 second polyelectrodialysis apparatus differs from that illustrated in Figure 4 in that the two
5 electrodialysis apparatus constituting the polyelectrodialysis apparatus are formed as a single stack of
6 compartment-forming elements of the kind described above. The electrodialysis apparatus are
7 arranged in the stack back-to-back, so that the cathode chamber 126 of one of the electrodialysis
8 apparatus is disposed juxtaposed the cathode chamber 226 of the other electrodialysis apparatus. A
9 central, water-impervious partition 200 partitions the two electrodialysis apparatus one from the other.
10 Water to be purified 150 is supplied to the first desalting compartment 136 of one of the
11 electrodialysis apparatus, then to the second desalting compartment 146 of the one apparatus. A feed
12 160 from the second desalting compartment 146 of the one apparatus is supplied to the second
13 desalting compartment 246 of the other electrodialysis apparatus, and subsequently to the first
14 desalting compartment 236 of the other electrodialysis apparatus. The water to be purified 150 thus
15 passes successively through a first cation exchange resin bed 137, a first anion exchange resin bed 147,
16 a second anion exchange resin bed 247 and a second cation exchange resin bed 237.

17
18 Substantially pure or pretreated water is supplied as a concentrating, flushing stream 256 to the
19 concentrating compartment 228 of the other electrodialysis apparatus and then to the concentrating
20 compartment 128 of the one electrodialysis apparatus, so that the concentrating stream flows through
21 the polyelectrodialysis apparatus in the opposite direction from the water to be purified 150. A
22 separate electrode rinsing stream 252 of high purity water is supplied to the anode compartment 224 of
23 the other electrodialysis apparatus, and then in parallel to the cathode compartments 126, 226 of the
24 one and other electrodialysis apparatus. The cathode rinsing streams are then recombined and passed
25 through the anode compartment 124 of the one electrodialysis apparatus. Thus, as with the
26 concentrating, flushing stream 256, the electrode rinsing stream is passed through the
27 polyelectrodialysis apparatus in the opposite direction to the water to be purified 150 (the desalting
28 stream). In this way, the back diffusion of impurity ions into the desalting stream is reduced.

29
30 Each of the electrode, concentrating and desalting compartments of the polyelectrodialysis apparatus
31 illustrated in Figure 5 has a thickness in the anode to cathode direction of about 15mm. When the
32 second polyelectrodialysis apparatus is operated for over 3500 hours with feed water of 10 to

1 20 μ S/cm, having 25 to 35 ppm dissolved carbon dioxide, at a rate of 1.0 to 1.5 litres per minute, the
2 resistivity of the product water 260 on exiting the stack is found to be in the range 15 to 17.5M Ω -cm.

3

4 As with the electrodialysis apparatus illustrated in Figures 2 and 3, the polyelectrodialysis apparatus
5 shown in Figures 4 or 5 may be modified so that the concentrating flushing stream and/or the electrode
6 rinsing streams are fed by a part of the product water which is returned through the apparatus.

7

8 In another variation, the central partition 200 of the second polyelectrodialysis apparatus may be
9 omitted, such that the apparatus includes a single, central cathode chamber. Said single cathode
10 chamber may include a single cathode or anode which is shared by the said one and other
11 electrodialysis apparatus.

12

13 The present invention thus provides an improved electrodialysis apparatus in which water to be
14 purified is passed successively through a cation exchange resin bed and an anion exchange resin bed
15 between an anode and a cathode. The anode and cathode are separated from the desalting stream by
16 cation and anion perm-selective membranes respectively, and the cathode and anode compartments are
17 filled with ion exchange resin material. Each of the electrode compartments is supplied with a feed of
18 substantially pure water, and in use the electrodialysis apparatus of the invention is found to give
19 product water of surprisingly high purity.

1 CLAIMS

2

3 1. An electrodialysis apparatus for purifying water, which apparatus comprises means defining an
4 anode chamber, means defining a cathode chamber, an anode means disposed within the anode
5 chamber, a cathode means disposed within said cathode chamber, means defining a desalting
6 stream flow path between said anode and said cathode means, means defining a concentrating
7 stream flow path adjacent said desalting stream flow path, means for causing or allowing water
8 to be purified to flow within the desalting stream flow path and means for causing or allowing
9 a fluid adapted to receive ionic impurities from the water to be purified to flow within the
10 concentrating stream flow path; wherein said desalting stream flow path comprises a first
11 portion juxtaposed the anode means and a second portion juxtaposed said cathode means, and
12 said means defining the desalting stream flow path comprises two first partition means that
13 separate the first portion of the desalting stream flow path from the anode chamber and the
14 concentrating stream flow path respectively, which first partition means are selectively
15 permeable to cations and are spaced apart on an axis between said anode means and cathode
16 means, and two second partition means that separate the second portion of the desalting
17 stream flow path from the cathode chamber and the concentrating stream flow path
18 respectively, which second partition means are selectively permeable to anions and are spaced
19 apart on said axis; characterised in that each of said anode and cathode chambers contains a
20 porous bed of ion exchange material.

21

22 2. An apparatus as claimed in Claim 1 wherein the ion exchange material in the cathode chamber
23 is an anion exchange resin.

24

25 3. An apparatus as claimed in Claim 1 or Claim 2 wherein the ion exchange material in the anode
26 chamber is a cation exchange resin.

27

28 4. An apparatus as claimed in any one of the preceding claims wherein the concentrating stream
29 flow path contains a porous bed of ion exchange material.

30

31 5. An apparatus as claimed in any one of the preceding claims wherein the first portion contains
32 cation exchange resin, and the second portion contains anion exchange resin.

1

2 6. An apparatus as claimed in any one of the preceding claims wherein water is caused or allowed
3 to flow through at least one of the anode chamber and cathode chamber.

4

5 7. An apparatus as claimed in Claim 6 wherein the water to flow through at least one of the
6 anode chamber and cathode chamber is water purified by the apparatus.

7

8 8. An apparatus as claimed in Claim 7 wherein the water to flow through at least one of the
9 anode chamber and cathode chamber is taken directly from the outlet water of the desalting
10 stream.

11

12 9. An apparatus as claimed in any one of Claims 6 to 8 wherein water is caused or allowed to
13 flow successively through the anode chamber and then the cathode chamber.

14

15 10. An apparatus as claimed in any one of Claims 6 to 9 wherein the water flow through at least
16 one of the anode chamber and cathode chamber subsequently flows through the concentrating
17 stream.

18

19 11. An apparatus as claimed in Claim 10 wherein a portion of the purified water prepared by the
20 apparatus flows sequentially through the anode chamber, the cathode chamber and the
21 concentrating stream.

22

23 12. An apparatus as claimed in any one of Claims 6 to 11 wherein water is caused or allowed to
24 flow in parallel through the concentrating stream and at least one of the anode and cathode
25 chambers.

26

27 13. An apparatus as claimed in any one of the preceding claims wherein the fluid within the
28 concentrating stream is caused or allowed to flow counter-current to the flow of water to be
29 purified in at least one of the first and second portions of the desalting streams flow paths.

- 1 14. An apparatus as claimed in anyone of the preceding claims wherein the water within at least
2 one of the anode and cathode chambers is caused or allowed to flow counter-current to the
3 flow of water to be purified in at least one of said first and second portions.
4
- 5 15. An apparatus as claimed in any one of the preceding claims wherein the water to be purified is
6 passed through the first portion first, followed by the second portion.
7
- 8 16. An apparatus as claimed in Claim 15 wherein the water to be purified flows in the same
9 direction through both portions.
10
- 11 17. An apparatus as claimed in any one of the preceding claims wherein the first desalting stream is
12 divided to form two or more sub-chambers, and wherein the desalting stream path flows in
13 succession through one of the sub-chambers of the first desalting compartment, then through
14 the second desalting compartment, and subsequently through a second sub-chamber of the
15 first desalting compartment.
16
- 17 18. An apparatus as claimed in any one of the preceding claims wherein the purified water has a
18 resistivity of at least $1\text{M}\Omega\text{-cm}$.
19
- 20 19. An apparatus as claimed in Claim 18 wherein the purified water has a resistivity of at least
21 $15\text{M}\Omega\text{-cm}$.
22
- 23 20. A method of electrodialysis comprising causing or allowing water to be purified to flow in the
24 desalting stream flow path of an electrodialysis apparatus as defined in any one of Claims 1 to
25 19, and causing or allowing a fluid adapted to receive ionic impurities from said water to be
26 purified to flow within the concentrating stream path and applying a voltage across the anode
27 means and cathode means.
28
- 29 21. A polyelectrodialysis apparatus comprising two or more electrodialysis apparatus as defined in
30 any one of Claims 1 to 19.

- 1 22. A polyelectrodialysis apparatus as claimed in Claim 21 wherein water to be purified through
2 two electro dialysis apparatus passes successively through the first and second portions of the
3 first electro dialysis apparatus, and then successively through the second and first portions of
4 the second electro dialysis apparatus.
5
- 6 23. A polyelectrodialysis apparatus as claimed in Claim 21 or Claim 22 wherein at least one of the
7 concentrating streams, anode chambers and cathode chambers are fed by a water purified by
8 the apparatus.
9
- 10 24. A polyelectrodialysis apparatus as claimed in any one of Claims 21 to 23 including a flow
11 through the anode chambers and cathode chambers, wherein at least one of the anode chamber
12 flows, cathode chamber flows and the concentrating stream flows flow firstly through the
13 second electro dialysis apparatus and subsequently through the first electro dialysis apparatus.
14
- 15 25. A polyelectrodialysis apparatus as claimed in any one of claims 21 to 24 wherein the outflow
16 from at least one of the anode chambers, cathode chambers and concentrating streams are
17 passed through a purifier for reuse in the apparatus.
18
- 19 26. A polyelectrodialysis apparatus as claimed in any one of Claims 21 to 25 wherein two or more
20 of the electro dialysis apparatus are juxtaposed to form a single stack.
21
- 22 27. A polyelectrodialysis apparatus as claimed in Claim 26 wherein two or more of the electrode
23 chambers are shared by two adjacent electro dialysis apparatus.

INTERNATIONAL SEARCH REPORT

Inter. .onal Application No

PCT/US 99/02552

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D61/48 C02F1/469

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | US 2 923 674 A (T. R. E. KRESSMAN) 2 February 1960 ESPECIALLY COLUMN 2, LINES 53-62 | 1 |
| A | US 3 014 855 A (T. R. E. KRESSMAN) 26 December 1961 see the whole document | 1 |
| A | US 3 084 113 A (D. J. VALLINO) 2 April 1963 see the whole document | 1 |
| A | US 4 787 561 A (G. KUNZ) 29 November 1988 see the whole document | 1 |
| A | DE 44 18 812 A (FORSCHUNGSZENTRUM JÜLICH GMBH) 7 December 1995 see the whole document | 1 |
| -/-- | | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Devisme, F

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | FR 1 282 890 A (AMERICAN MASCHINE & FOUNDRY CO.) 15 June 1962 see the whole document ----- | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. No.

PCT/US 99/02552

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US 2923674 A | 02-02-1960 | GB 879181 A | |
| US 3014855 A | 26-12-1961 | GB 882601 A | |
| US 3084113 A | 02-04-1963 | NONE | |
| US 4787561 A | 29-11-1988 | NONE | |
| DE 4418812 A | 07-12-1995 | WO 9532791 A | 07-12-1995 |
| | | EP 0762927 A | 19-03-1997 |
| | | JP 10500895 T | 27-01-1998 |
| FR 1282890 A | 15-06-1962 | NONE | |